Neutral Macrocyclic Boxes Spontaneously Assembled from Osmium Tetraoxide, Olefin, and Pyridyl Ligand

Kyu-Sung Jeong,* Young Lag Cho, Jeong Uk Song, Hong-Young Chang, and Moon-Gun Choi

Department of Chemistry, Yonsei University Seoul 120-749, Korea

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Self-assembly is now recognized as a highly efficient strategy for the construction of supramolecular species or receptors where suitable subunits are held together by noncovalent interactions.[1] The elegant examples to date have been generated by exploiting the hydrogen bond[1,2] as well as the metal−ligand coordinate bond[1,3,4] in a controlled fashion. Over the past few years, Fujita et al.[3] and Stang et al.[4] have reported a variety of discrete, structurally well-defined cationic molecular boxes using square-planar transition metals, Pd(II) and Pt(II), that provide approximately 90° bond angles at the corners. Of great challenge yet importance is to design and discover a new combination of transition metal, ligand, and other components that can assemble themselves to form discrete, stable supramolecular complexes with a well-defined geometry and cavity. Herein we describe for the first time self-assembly of the *discrete*, *neutral*, and *octahedral* osmium(VI) ester-bridged macrocyclic box.

Addition of the osmium tetraoxide (1 equiv) to a 1:1 stoichiometric mixture of the bispyridyl ligands **1a**−**e**[5] and 2,3-dimethyl-2-butene in toluene at room temperature resulted in the precipitation of brown solids within a few minutes via the combination of osmylation and coordination between the reactants (Scheme 1). The reaction essentially proceeds quantitatively, but the isolated yields are 82−97%. The products are air-stable, moisture-insensitive, and soluble in various organic solvents including dichloromethane, chloroform, tetrahydrofuran, acetone, and dimethyl sulfoxide. The elemental analysis of the solid agreed well with 1:1:1 molar composition of osmium tetraoxide, olefin, and bispyridyl ligand. The FAB mass spectra with isotopic distribution patterns[6] are consistent with the macrocycles **2a**−**e**. The infrared spectra of **2a**−**e** show a strong, characteristic band near 830 cm^{-1} diagnostic of the trans O═Os═O moiety of the octahedral dioxoosmium(VI) complexes.[7] The ^{1}H NMR signals for the hydrogens α to the pyridyl nitrogen of **2a**−**e** were downfield shifted (0.2−0.3 ppm) in a variety of solvents (CD_2Cl_2, $CDCl_3$, CD_3CN, and DMSO-d_6) relative to those for free ligands, as expected for the coordination of the pyridyl nitrogen to the metal, Os(VI). In addition, the ^{1}H NMR spectra of **2a**−**e** remained nearly constant in a wide concentration range (0.25−20 mM) in $CDCl_3$.[8]

Furthermore, the discrete binuclear structure was confirmed by X-ray diffraction studies of complex **2b**·4(1-naphthol)[9,10] as well as macrocycle **2e**.[11] As shown in Figure 1, **2b** is a

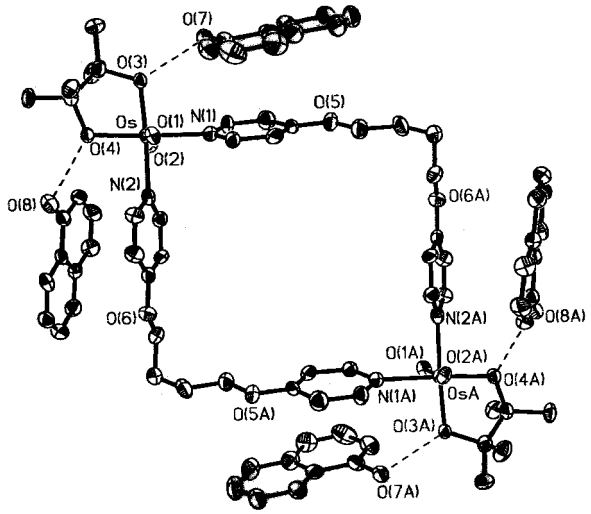
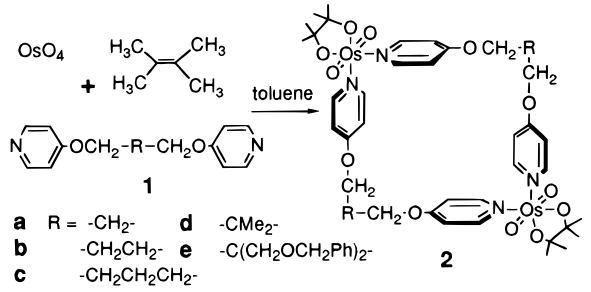


Figure 1. X-ray crystal structure of **2b**·4(1-naphthol). Hydrogen atoms have been omitted for clarity.

Scheme 1



* To whom correspondence should be addressed. E-mail: ksjeong@alchemy.yonsei.ac.kr.

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(6) See Supporting Information.

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(8) New minor signals could be seen, however, at relatively higher concentrations of the macrocycles **2**, especially **2c** having a longer and more flexible linker; see Supporting Information.

(9) The single crystals of the complex **2b**·4(1-naphthol) were grown by slow evaporation over 1 week of a $CHCl_3$ solution of **2b** containing ~8 molar equiv of 1-naphthol. Crystal data: monoclinic, $P2_1/c$; a = 13.6634(7), b = 18.4047(10), c = 14.89875(8); β = 91.477(1)°; V = 3745.0(3) Å^3; z = 2; D_{calcd} = 1.541 g cm^{-3}; $F(000)$ = 1744; λ (Mo Kα) = 0.710 73 Å; temp, 296(1) K; crystal size, 0.51 × 0.31 × 0.21 mm; reflections collected/unique, 15 636/5380 (R(int) = 0.1213); 464 parameters; final R indices ($I > 2\sigma(I)$) R = 0.0445, R_w = 0.0891; R indices (all data) R = 0.0657, R_w = 0.0963.

(10) Addition of 1-naphthol to a $CDCl_3$ solution of **2b** caused the aryl and −OCH_2− signals of **2b** to shift upfield gradually up to $\Delta\delta$ = 0.6 ppm, and precipitation occurs on prolonged standing (>30 min). The ^{1}H NMR integration of the precipitates gave a 1:4 ratio of **2b** and 1-naphthol.

(11) For the X-ray structure and crystallographic data of **2e**, see Supporting Information.

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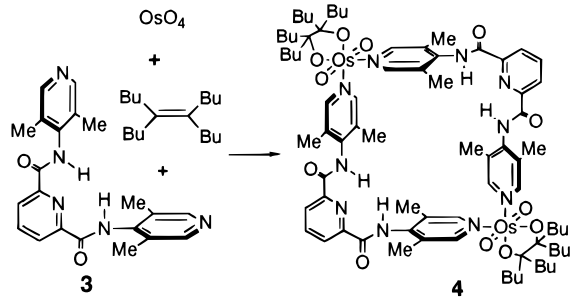
Scheme 2



rectangular box with a 8.59(1) × 9.69(1) Å edge-to-edge distance (osmium to carbon at the each corner), and the geometry at the Os(VI) center is distorted octahedral, where the O═Os═O bond angle is 162.9(2)°. In addition, the N−Os−N bond angle is 89.5-(2)°, approximately an ideal right angle for self-assembly of molecular squares or rectangles. The naphthols in the complex **2b**·4(1-naphthol) are held together by the combination of OH···O hydrogen bonding and face-to-face aryl stacking interaction. The interplane distance between the naphthyl and pyridyl rings is 3.48 ± 0.06 Å. It is also noteworthy that the OH group of naphthol is hydrogen-bonded (O···O distance 2.69 ± 0.06 Å) to each of all four oxygens of the Os−O−C bonds, not of the Os═O bonds.

To illustrate the versatility of our novel self-assembling motif, the functionalized molecular receptor **4**,[12] containing two hydrogen-bonding sites at the diagonal corners, was prepared by employing pyridine-2,6-dicarboxamide ligand **3** and a readily soluble olefin, 5,6-dibutyl-5-decene (Scheme 2).[13] The ^{1}H NMR signals for aryl hydrogens in the lutidine rings of ligand **3** were downfield-shifted by ∼0.2 ppm as expected for the coordination. The ^{1}H NMR spectrum of receptor **4** remained unchanged in a wide concentration range (0.25−10 mM in $CDCl_3$),[14] suggesting that no significant structural variation and aggregation occur.

The binding property of **4** with carboxamides was studied in $CDCl_3$ by ^{1}H NMR spectroscopy. As shown in Figure 2, addition of terephthalamide **5** to a solution of **4** resulted in a large downfield shift ($\Delta\delta \sim 1.2$ ppm) of the amide NHs, indicating strong hydrogen bond formation. More interestingly, the aryl protons of the guest **5** were highly upfield-shifted from 7.4 to 5.4 ppm. Furthermore, the separated signals could be seen for free and bound guests upon lowering the temperature down to −40 °C. Nonlinear least-squares fitting analysis[15] of the ^{1}H NMR titration curve revealed a large association constant of (2.0 ± 0.5) × 10^4 M^{-1} between **4** and **5** in $CDCl_3$ at 296 ± 0.5 K. This value is much higher than the association constants of **4** with *trans*-cyclohexane-1,4-dicarboxamide **6** (910 ± 15 M^{-1}), isophthalamide **7** (<5 M^{-1}), and benzamide **8** (9 ± 3 M^{-1})[16] under the same conditions. These results suggest that the magnitude of the association constants strongly depends on the relative position of the guest functional groups as well as steric fitness into the cavity. The Job's plots[17] showed that maximal complexation occurred at ∼0.5 molar fraction of receptor **4** and the guests, **5** and **6**, indicating that 1:1 bindings occur. Additionally, in the NOE difference experiment of a 1:1 molar mixture of **4** and **5**, the enhancement (∼0.85%) of the aryl signal of the lutidine rings was observed on irradiation of the guest aryl protons. All of the observations described above support the proposed structure of complex **9**, where the guest **5** is complexed inside the cavity of receptor **4** mainly through the hydrogen bonding interaction between the receptor NHs and the guest carbonyl oxygens.

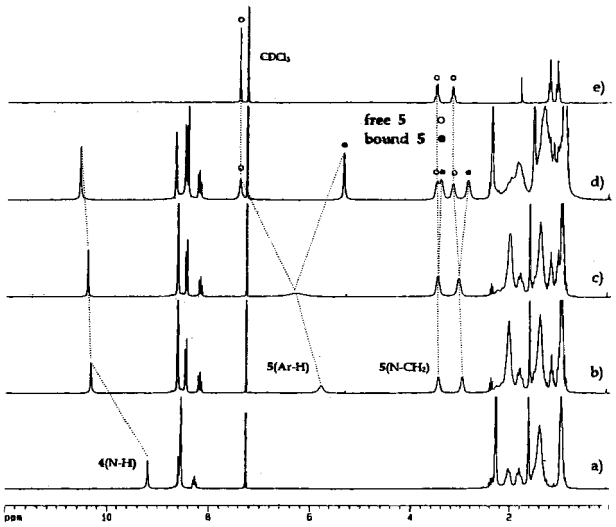
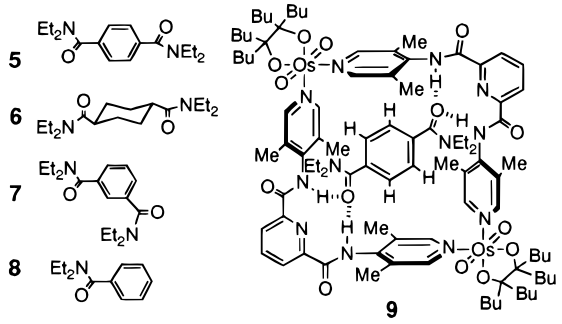


Figure 2. ^{1}H NMR spectra of (a) **4** (5.0 mM) at 23 °C, (b) **4** (5.0 mM) + **5** (5.0 mM) at 23 °C, (c) **4** (5.0 mM) + **5** (7.5 mM) at 23 °C, (d) **4** (5.0 mM) + **5** (7.5 mM) at −40 °C, and (e) **5** (5.0 mM) at −40 °C.



A new system of self-assembly described herein is a great extension to the chemistry of discrete molecular and supramolecular assemblies driven by the metal−ligand coordinate bond. More elaborate supramolecular species with designed architecture and cavity can be prepared since a large number of olefins as well as ligands with a specific shape and functionality are easily accessible. We are currently extending further our investigation to this direction.

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Supporting Information Available: Preparation methods, elemental analyses, spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS), ^{1}H NMR spectra at various concentrations of **2a**−**e** and **4**, crystallographic data of **2b**·4(1-naphthol) and **2e**, and titration curves and Job's plots (56 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) Hunter and Sarson reported the self-assembly of a dimeric zinc−porphyrin host containing the same hydrogen bonding sites which selectively bound terephthalic acid derivatives with K_a = ∼1400 M^{-1} in $CDCl_3$, see: Hunter, C. A.; Sarson, L. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* (22), 2313−2316.

(13) Insoluble precipitates in various organic solvents including CH_2Cl_2, $CHCl_3$, DMSO, and nitrobenzene were formed when 2,3-dimethyl-2-butene was used instead. For preparation of tetraalkyl substituted olefins, see: Lenoir, D. *Synthesis* **1989**, 883−897.

(14) For the ^{1}H NMR spectra in various concentrations, elemental analysis, and FAB mass spectrum of **4**, see Supporting Information.

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(16) During titrations of receptor **4** with guests **7** and **8**, the magnitudes of chemical shift changes of the amide NH were too small ($\Delta\delta_{max} \sim 0.1$ ppm) to determine the association constants accurately in $CDCl_3$.

(17) Connors, K. A. *Binding Constants*; John Wiley & Sons: New York, 1987; p 24.